THERMODYNAMIC BEHAVIOUR OF A GASEOUS ASSEMBLY OF POINT-MOLECULES ASSUMING ASSOCIATION*

By M. DUTTA

(*Received for publication, April* 19, 1951)

ABSTRACT. In nature, for many gases, *viz*, sulphur vapour, water vapour, etc., there is decisive evidence of associations of molecules, yielding higher polymers. Here, on starting from some well-known results previously obtained by Darwin-Fowler method, various properties of the assembly, *viz*., isothermal and adiabatic compressibilities, coefficient of expansion, etc., have been investigated and have been expressed in terms of degree of associations such that an estimation can also be made from measurements of these quantities. Many of those properties have remarkable deviations from those of ideal gases in a direction, opposite to that of usual real gases. These peculiarities have also been justified qualitatively from Le Chatelier and Braun's principle.

INTRODUCTION

In usual investigations of properties of ideal gases, either by thermodynamic or by statistical methods, no consideration is taken for associations of molecules, *i.e.*, constituent particles are assumed to exist in the simplest form. But, in nature, for many gases, *viz.*, sulphur vapour, NO_2, water vapour (near about the boiling-point), iodine vapour, oxygen in presence of ozone, etc., in some suitable temperature-range, it has been found conclusively that there exists varying degree of association. Now Darwin-Fowler method is very suitable for discussion of behaviour of assemblies in which constituent particles are associating and dissociating. Starting from some well-known results obtained by this method, the isothermal compressibility for an assembly of point molecules, assuming associations, has been obtained and proved to be greater than that for ideal gases composed of molecules of permanent type. This conclusion has also been shown to be plausible in a qualitative manner from a discussion based on Le Chatelier and Braun's principle. The expression for isothermal compressibility has been written in a form, appearing to be suitable for determining degree of dissociation (or better association) from measurements on isothermal compressibility. After this, expression for coefficient of volume-expansions, C_p, C_v, γ etc., have been calculated for assembly of this type. Finally, the expression for velocity of propagation of sound through gases of this type has been obtained, and this, after putting in suitable form, appears to be useful for determining degree of association by measuring velocity of propagation of sound in gases of this type under consideration.

* Communicated by Prof. S. N. Bose.

DESCRIPTION OF THE ASSEMBLY

For simplicity, it has been assumed that the assembly is composed of molecules, essentially of the same type, existing in the simplest form, or in form of simply associated polymers. Thus, if X represents the molecule in the simplest form, then the assembly consists of $(X)_1$, $(X)_2$,...$(X)_r$,...$(X)_n$, where the suffix 'r' represents the number of molecules, associated in forming polymers of r-order. Let N_1, N_2,...N_n be the average number of $(X)_1$, $(X)_2$, ...$(X)_n$ polymers in the assembly, and so

$$\Sigma rN_r = A \qquad \ldots \quad (1)$$

where A is the total number of X molecules present in the assembly. Again, if N represents total number of molecules existing in free state in the volume, then

$$\Sigma N_r = A \qquad \ldots \quad (2)$$

SOME IMPORTANT WELL-KNOWN RESULTS

Now, the thermodynamic probability in the Darwin-Fowler sense is

$$C = \frac{1}{(2\pi i)^2} \int_\Gamma \int_\Gamma \frac{dz}{z^{E+1}} \frac{dt}{t^{A+1}} \exp\{P_1(z_1)t + P_2(z_1)t^2 + \ldots + P_n(z_1)t^n\} \qquad \ldots \quad (3)$$

where $P_r(z) =$ partition function of polymer $(X)_r$

$$= \left\{ \frac{2\pi m_r}{\log (1/z)} \right\}^{\frac{3}{2}} \frac{V}{h^3} \cdot z^{\chi_n + rb}$$

$$= P(z) \cdot r^{\frac{3}{2}} \cdot z^{\chi_r + rb}, \qquad \ldots \quad (4)$$

on writing

$$P(z) = \left(\frac{2\pi m}{\log (1/z_1)} \right)^{\frac{3}{2}} \cdot \frac{V}{h^3} \qquad \ldots \quad (5)$$

In the above expressions, V is the volume of the assembly m_r is mass of $(X)_r$, and m is mass of (X), 'b' the rest energy, χ_r the binding energy of r molecules in polymers of rth type, and, here, it is taken as

$$m_r = rm$$

So, the above can be written as

$$C = \frac{1}{(2\pi i)^2} \int_\Gamma \int_\Gamma \frac{dz_1}{z^{E+1}} \frac{dt}{t^{A-1}} \exp\{P(z)Q(t, z)\} \qquad \ldots \quad (6)$$

where

$$Q(t, z) = tz^b + z^{\frac{3}{2}} \cdot t^2 z^{2b+\chi_2} + 3^{\frac{3}{2}} \cdot t^3 \cdot z^{3b+\chi_3} + \ldots + n^{\frac{3}{2}} t^n z^{nb+\chi_n} \qquad \ldots \quad (7)$$

Now, by the method of steepest descent, the approximating value of C is given by

$$C=\frac{\exp\{P(z_0)Q(t_0,\ z_0)\}}{t_0{}^{A}z_0{}^{E}} \qquad \ldots \quad (8)$$

where t_0, z_0 are determined from the equations,

$$E=Q(t_0,\ z_0)z_0\frac{\delta P}{\delta z_0}+P(z_0)z_0\frac{\delta Q(t_0,\ z_0)}{\delta z_0} \qquad \ldots \quad (9)$$

and

$$A=P(z_0)t_0\frac{\delta Q(t_0,\ z_0)}{\delta t_0}$$

$$=P(z_0)Q_1(t_0,\ z_0) \qquad \ldots \quad (10)$$

where

$$Q_1(t_0,\ z_0)=t_0z_0^{b}+2^{5/2}t_0^{2}z^{2b+\chi_2}+\ldots+n^{5/2}t_0^{n}z_0^{nb+\chi_n} \qquad \ldots \quad (11)$$

Now, as shown by Darwin and Fowler, we have

$$\left.\begin{aligned} z_0&=e^{-\mu/kT}\\ t_0&=e^{\Psi/kT}\\ N_r&=t^rP_r(z_0)\end{aligned}\right\} \qquad \ldots \quad (12)$$

and $$p=\frac{kT}{V}(\Sigma N_r)=\frac{kT}{V}\left\{\Sigma t^rP_r(z_0)\right\}=\frac{kT}{V}P(z_0)Q(t_0,\ z_0) \qquad \ldots \quad (13)$$

where p is the pressure, T the temperature of the assembly, ψ is the partial thermodynamic potential and k the Boltzmann constant. The equation of state is same as that for mixture of ideal gases.

ISOTHERMAL COMPRESSIBILITY

Now, if p and T are taken as independent thermodynamic variables of the system, then, from the above, we see that V, t_0, etc., are functions of p, T both, and, z_0 and so, $P(z_0)/V$ of T alone. Then, on differentiating the equation (11) partially with respect to p, it becomes

$$\frac{1}{p}=\frac{1}{Q(t_0,\ z_0)}\cdot\frac{\delta Q(t_0,\ z_0)}{\delta t_0}\left(\frac{\delta t_0}{\delta p}\right.$$

$$\text{or}\quad \frac{1}{t_0}\left(\frac{\delta t_0}{\delta p}\right)_T=\frac{Q(t_0,\ z_0)}{Q_1(t_0,\ z_0)}\cdot\frac{1}{p} \qquad \ldots \quad (14)$$

$$\ldots \quad (15)$$

$$AkT$$

On differentiating partially and logarithmically the equation (10), it becomes

$$-\frac{1}{V}\left(\frac{\delta V}{\delta p}\right)_T = \frac{1}{Q_1(t_0, z_0)}\left\{\frac{\delta}{\delta t_0} Q_1(t_0, z_0)\right\}\left(\frac{\delta t_0}{\delta p}\right)_T$$

$$= \frac{1}{p}\frac{Q(t_0, z_0)Q_2(t_0, z_0)}{\{Q_1(t_0, z_0)\}^2} \quad \ldots \quad (16)$$

after substituting the value of $\frac{1}{t_0}\left(\frac{\delta t_0}{\delta p}\right)_T$ from the equation (11) where

$$Q_2(t_0, z_0) = t_0 \frac{\delta}{\delta t_0} Q_1(t_0, z_0)$$

From the equation (12), they become

$$P(z_0)Q(t_0, z_0) = \sum N_r$$

$$P(z_0)Q_1(t_0, z_0) = \sum rN_r = A$$

$$P(z_0)Q_2(t_0, z_0) = \sum r^2 N_r$$

$$\therefore \quad -\frac{1}{V}\left(\frac{\delta V}{\delta p}\right)_T = \frac{1}{p}\frac{(\sum N_r)(\sum r^2 N_r)}{\{\sum rN_r\}^2}$$

$$= \frac{1}{p}\left[1 + \frac{(\sum N_r)(\sum r^2 N_r) - (\sum rN_r)^2}{(\sum rN_r)^2}\right]$$

$$= \frac{1}{p}\left[1 + \frac{\sum_r \sum_m (r-m)^2 N_r N_m}{(\sum rN_r)^2}\right] \leq \frac{1}{p} \quad \ldots \quad (18)$$

Now, for an ideal gas at the same temperature and pressure, the compressibility is equal to $1/p$. Thus, the system is more compressible than an ideal gas at the same temperature and pressure, though both of them satisfy the equation of state of the same form.

Now, the equation (17) can be put in a very useful form as follows

$$-\frac{1}{V}\left(\frac{\delta V}{\delta p}\right)_T = \frac{1}{p}\left[1 + \sum_{r \neq m}\sum \frac{(r-m)^2}{rm} \xi_r \xi_m\right] \quad \ldots \quad (19)$$

where

$$\xi_r = \frac{rN_r}{A} = \frac{\text{number of constituent molecules } (X) \text{ associated to form polymer } (X)}{\text{total number of constituent molecules } (X) \text{ present in assembly}}$$

In the simplest case, where polymers of the type $(X)_2$ only exists, as in the assemblies of NO_2 and N_2O_4, or of I and I_2, the equation (18) reduces to the following form

$$-\frac{1}{V}\left(\frac{\delta V}{\delta p}\right) = \frac{1}{p}\left[1 + \tfrac{1}{2}\xi_1 \xi_2\right] \quad \ldots \quad (20)$$

where

$$\xi_1 = \frac{N_1}{A} = \xi, \; \xi_2 = \frac{2N_2}{A} = 1 - \xi \qquad \ldots \quad (21)$$

and ξ may be called as degree of association.

Then,

$$-\frac{1}{V}\left(\frac{\delta V}{\delta p}\right)_T = \frac{1}{p}\left[1 + \tfrac{1}{2}\xi(1-\xi)\right] \qquad \ldots \quad (22)$$

For the range of temperature and pressure when $\xi = 0$ or $\xi = 1$, the compressibility, as expected, (since the assembly reduces to that of ideal gases), is equal to $1/p$.

The maximum deviation occurs when $\xi = \frac{1}{2}$ and is equal to $12\frac{1}{2}$ %.

SOME REMARKS BASED ON LE CHATELIER AND BRAUN'S PRINCIPLE

Now, the principle of Le Chatelier and Braun asserts that the increase of a generalised force Y_i (*i.e.*, intensity) produces a displacement of equilibrium attended by a process (transformation or chemical reaction) in which the change of the conjugate variables ΔX_i is positive (Epestein, 1947).

So, when the pressure is increased, chemical reaction will take place in such a way that the conjugate variable $(-\Delta V)$ is positive, *i.e.* volume decreases. Evidently more association of molecules cause a decrease in volume. So, with increase of pressure, there will be more association in the system. This will yield some positive contribution to the compressibility over and above the usual compressibility expected for ordinary ideal gas. Thus, the gas of the type considered here is more compressible than the ordinary ideal gas at some temperature and pressure.

ISOTROPIC COEFFICIENT OF EXPANSION

Now, on differentiating the equation (11) with respect to T after keeping p constant, the following is obtained :

$$O = \frac{1}{T} + \left\{\tfrac{3}{2}kT + \frac{QZ'(t_0, z_0)}{Q(t_0, z_0)}\right\}\left\{z_0 \frac{\delta z_0}{\delta T} + \frac{Q_1(t_0, z_0)}{Q(t_0, z_0)} \frac{1}{t_0}\left(\frac{\delta t_0}{\delta T}\right)_p\right.$$

where

$$QZ'(t_0, z_0) = z_0 \frac{\delta Q(t_0, z_0)}{\delta z_0} \qquad \ldots \quad (24)$$

$$\frac{1}{t_0}\left(\frac{\delta t_0}{\delta T}\right)_p = -\tfrac{5}{2}\frac{Q(t_0, z_0)}{Q_1(t_0, z_0)} \frac{1}{T} - \frac{QZ'(t_0, z_0)}{Q_2(t_0, z_0)} \cdot \frac{1}{kT^2} \qquad \ldots \quad (25)$$

On taking p, T as variables and on differentiating the equation (10) logarithmically and partially with respect to T, the following is obtained :

$$-\frac{1}{V}\left(\frac{\delta V}{\delta T}\right)_p = \left[\frac{z_0\frac{\delta}{\delta z_0}\left\{\frac{P(z_0)}{V}\right\}}{P(z_0)/V} + \frac{Q_1Z'(t_0, z_0)}{Q_1(t_0, z_0)}\right]\frac{1}{z_0}\frac{\delta z_0}{\delta T} + \frac{Q_2(t_0, z_0)}{Q_1(t_0, z_0)}\cdot\frac{1}{t_0}\left(\frac{\delta t_0}{\delta T}\right)_p$$

where

$$Q_1Z'(t_0, z_0) = z_0\frac{\delta Q_1(t_0, z_0)}{\delta z_0} \qquad \ldots \quad (26)$$

On the substitution of the value of $\frac{1}{t_0}\left(\frac{\delta t_0}{\delta T}\right)_p$ from (25) the above becomes

$$\begin{aligned}\frac{1}{V}\left(\frac{\delta V}{\delta T}\right)_p &= \tfrac{5}{2}\frac{Q_2Q}{Q_1^2}\cdot\frac{1}{T} + \frac{Q_2QZ'}{Q_1^2}\cdot\frac{1}{kT^2} - \tfrac{3}{2}\frac{1}{T} - \frac{Q_1Z'}{Q_1}\frac{1}{kT^2}\\ &= \frac{1}{T}\left[1 + \tfrac{5}{2}\frac{\sum\sum(r-m)^2N_rN_m}{A^2}\right.\\ &\quad \left. + \frac{1}{kT}\frac{\{\sum r^2N_r\}\{\sum N_r(\chi_r + rb)\} - \{\sum N_r r(\chi_r + b)\}\{\sum rN_r\}}{A^2}\right]\\ &= \frac{1}{T}\left[1 + \tfrac{5}{2}\sum\sum\frac{(r-m)^2}{rm}\xi_r\xi_m + \sum\sum\frac{(r-m)}{rm}\xi_r\xi_m\left(\frac{r\chi_m}{kT} - \frac{m\chi_r}{kT}\right)\right]\end{aligned}$$

$$\ldots \quad (27)$$

In the simple case, where polymers of the type $(X)_2$ only exist, the expression becomes

$$\frac{1}{V}\left(\frac{\delta V}{\delta T}\right)_p = \frac{1}{T}\left[1 + \tfrac{1}{2}\xi(1-\xi)\left(\tfrac{5}{2} - \frac{\chi}{kT}\right)\right] \leq \frac{1}{T} \qquad \ldots \quad (28)$$

if

$$\frac{\chi}{kT} < \tfrac{5}{2}.$$

SPECIFIC HEAT AT CONSTANT PRESSURE

Now, according to the equation (9) the total energy is

$$\begin{aligned}E &= \tfrac{3}{2}kTP(z_0)Q(t_0, z_0) + P(z_0)QZ'(t_0, z_0)\\ &= \tfrac{3}{2}kT[\sum N_r] + \sum N_r(\chi_r + rb)\end{aligned}$$

On differentiating this partially with respect to T, this becomes

$$\left(\frac{\delta E}{\delta T}\right)_p = \tfrac{3}{2}kP(z_0)Q(t_0, z_0) + \left[z_0\frac{\delta}{\delta z_0}\left\{\frac{P(z_0)}{V}\right\}\left\{\tfrac{3}{2}kTQ(t_0, z_0) + QZ'(t_0, z_0)\right\}V\right.$$

$$\left. + \tfrac{3}{2}kTP(z_0)QZ'(t_0, z_0) + P(z_0)QZ'Z'(t_0, z_0)\right]\frac{1}{z_0}\frac{\delta z_0}{\delta T}$$

$$+ \left[\tfrac{3}{2}kTP(z_0)Q(t_0, z_0) + P(z_0)QZ'(t_0, z_0)\right] \frac{1}{V}\left(\frac{\delta V}{\delta T}\right)_p$$

$$+ \left[\tfrac{3}{2}kTP(z_0)Q_1(t_0, z_0) + P(z_0)Q_1Z'(t_0, z_0)\right] \frac{1}{t_0}\left(\frac{\delta t_0}{\delta T}\right)_p$$

$$= \tfrac{3}{2}kP(z_0)Q(t_0, z_0) + \left[\tfrac{9}{4}kTP(z_0)Q(t_0, z_0) + 3P(z_0)QZ'(t_3, z_0) + P(z_0)QZ'Z'(t_0, z_0)\right] \frac{1}{T}$$

$$+ \left[\tfrac{3}{2}kTP(z_0)Q(t_0, z_0) + P(z_0)QZ'(t_0, z_0)\right]\left[\left\{\frac{\tfrac{5}{2}Q_2(t_0, z_0)Q(t_0, z_0)}{[Q_1(t_0, z_0)]^2} - 3\right\}\frac{1}{2}\frac{1}{T} + \frac{Q_2QZ' - Q_1Z'Q_1}{kT^2Q_1^2}\right]$$

$$- \left[\tfrac{3}{2}kTP(z_0)Q_1(t_0, z_0) + P(z_0)Q_1Z'(t_0, z_0)\right]\left[\frac{5}{2}\frac{1}{T}\frac{Q(t_0, z_0)}{Q_2(t_0, z_0)} + \frac{QZ'(t_0, z_0)}{Q_1(t_0, z_0)}\frac{1}{kT^2}\right]$$

after substituting the values of $\frac{1}{t_0}\left(\frac{\delta t_0}{\delta T}\right)_p$, $\frac{1}{V}\left(\frac{\delta V}{\delta T}\right)_p$, from (25) and (27).

Then

$$C_p = \left(\frac{\delta E}{\delta T}\right)_p + p\left(\frac{\delta V}{\delta T}\right)_p$$

$$= -\frac{15}{4}kP(z_0)Q(t_0, z_0) - \frac{5P(z_0)Q(t_0, z_0)}{T}\cdot\frac{Q_1Z'(t_0, z_0)}{Q_1(t_0, z_0)}$$

$$- \frac{2}{kT^2}\frac{P(z_0)Q_1Z'(t_0, z_0)Q(Z't_0, z_0)}{Q_1(t_0, z_0)} + \frac{P(z_0)QZ'Z'(t_0, z_0)}{kT^2}$$

$$+ \frac{1}{T}\left[\tfrac{5}{2}kTPQ + p(z_0)QZ'(t_0, z_0)\right]\left[\frac{Q_2(t_0, z_0)\left\{\frac{5}{2}Q(t_0, z_0) + \frac{QZ'(t_0, z_0)}{kT}\right\}}{\{Q_1(t_0, z_0)\}^2}\right]$$

$$= Ak\left[-\frac{15}{4}\left(\sum\frac{\xi_r}{r}\right) - 5\left(\sum\frac{\xi_r}{r}\right)\left(\sum\frac{\xi_r}{r}\frac{\chi_r + rb}{kT}\right) - 2\left(\sum\xi_r\frac{\chi_r + rb}{kT}\right)\left(\sum_1^{\xi_r}\frac{\chi_r + rb}{kT}\right)\right.$$

$$+ \sum\frac{\xi_r}{r}\left(\frac{\chi_r + rb}{kT}\right)^2 + \left(\frac{5}{2}\sum\frac{\xi_r}{r} + \sum\frac{\xi_r}{r}\frac{\chi_r + rb}{kT}\right)\left\{\left(\sum_1\xi_r\right)\left(\frac{5}{2}\sum\frac{\xi_r}{r}\right.\right.$$

$$\left.\left.\left.+ \sum\frac{\xi_r}{r}\frac{\chi_r + rb}{kT}\right)\right\}\right] \quad \ldots \quad (29)$$

Now, in the simplest case, referred to above, [where polymers of the type $(X)_2$ only exist], this reduces to

$$C_p = Ak\left[-\frac{15}{4}\frac{(1+\xi)}{2} - \frac{5}{2}\frac{1+\xi}{2}\left\{\frac{\xi b}{kT} + \frac{1-\xi}{2}\frac{\chi+2b}{kT}\right\}\right.$$

$$-2\left\{\frac{\xi b}{kT} + \frac{1-\xi}{2}\frac{\chi+2b}{kT}\right\}\left\{\frac{\xi b}{kT} + (1-\xi)\frac{\chi+2b}{kT}\right\}$$

$$+\left\{\frac{5}{2}\frac{1+\xi}{2} + \xi\frac{b}{kT} + \frac{1-\xi}{2}\frac{\chi+2b}{kT}\right\}\left\{(2-\xi)\left(\frac{1+\xi}{2}\cdot\frac{5}{2} + \frac{\xi b}{kT} + \frac{1-\xi}{2}\frac{\chi+2b}{kT}\right)\right\}$$

$$\left.+\left\{\frac{\xi b^2}{(kT)^2} + \frac{(1-\xi)}{2}\left(\frac{\chi+2b}{kT}\right)^2\right\}\right] \qquad \ldots (29a)$$

ISOTHERMAL ELASTICITY

To calculate the isothermal elasticity and the specific heat at constant volume, V and T are to be taken as independent variables.

On differentiating the equation (10) partially with respect to V, the following relation is obtained :

$$-\frac{A}{V^2} = \frac{P(z_0)}{V}Q_2(t_0, z_0).\frac{1}{t_0}\left(\frac{\delta t_0}{\delta V}\right)_T$$

$$\text{or} \quad -\frac{1}{t_0}\left(\frac{\delta t_0}{\delta V}\right)_T = \frac{A}{V}\frac{1}{P(z_0)Q_2(t_0, z_0)} \qquad \ldots (30)$$

Now, on differentiating (13) with respect to V and keeping T constant, the expression for isothermal elasticity is obtained as :

$$-V\left(\frac{\delta p}{\delta V}\right)_T = -kTP(z_0)Q_1(t_0, z_0)\frac{1}{t_0}\left(\frac{\delta t_0}{\delta V}\right)_T$$

$$= \frac{A^2kT}{V}\frac{1}{P(z_0)Q_2(t_0, z_0)}$$

$$= kT\frac{P(z_0)}{V}Q(t_0, z_0)\Big/\frac{Q(t_0, z_0)Q_1(t_0, z_0)}{Q_1(t_0, z_0)}$$

$$= p/\{1 + \sum\sum\frac{(r-m)^2}{rm}\xi_r\xi_m\} \leq p \qquad \ldots (31)$$

In this connection, it is to be remembered that for ideal gas, this is equal to p.

SPECIFIC HEAT AT CONSTANT VOLUME

On differentiating the equation (10) partially with respect to T, keeping V constant, the following relation is obtained :

$$O=\tfrac{3}{2}kTP(z_0)Q_1(t_0, z_0)\frac{1}{kT^2}+P(z_0)Q_1Z'(t_0, z)\frac{1}{kT^2}$$

$$+P(z_0)Q_2(t_0, z_0)\frac{1}{t_0}\left(\frac{\delta t_0}{\delta T}\right)_V$$

or
$$\frac{1}{t_0}\left(\frac{\delta t_0}{\delta T}\right)_V=-\frac{1}{T}\left\{\frac{3}{2}\frac{Q_1(t_0, z_0)}{Q_2(t_0, z_0)}+\frac{1}{kT}\frac{Q_1Z'(t_0, z_0)}{Q_2(t_0, z_0)}\right\} \quad \ldots (32)$$

Then, on differentiating the equation (9) partially with respect to T and, on substituting the value of $\frac{1}{t_0}\left(\frac{\delta t_0}{\delta T}\right)_V$ the expression for the specific heat at constant volume is obtained as

$$C_v=\tfrac{3}{2}kP(z_0)Q(t_0, z_0)+\frac{1}{T}\left[\frac{9}{4}kTP(z_0)Q(t_0, z_0)+3P(z_0)QZ'(t_0, z_0)\right.$$

$$\left.+\frac{P(z_0)QZ'Z'(t_0, z_0)}{kT}\right]$$

$$-\frac{1}{T}\left[\tfrac{3}{2}kTP(z_0)Q_1(t_0, z_0)+P(z_0)Q_1Z'(t_0, z_0)\right]\left[\frac{3}{2}\frac{Q_1(t_0, z_0)}{Q_2(t_0, z_0)}\right.$$

$$\left.+\frac{1}{kT}\frac{Q_1Z'(t_0, z_0)}{Q_2(t_0, Z_0)}\right]$$

$$=Ak\left[\frac{15}{4}\sum\frac{\xi_r}{r}+3\sum\xi_r\left(\frac{\chi_r+rb}{kT}\right)+\sum\frac{\xi_r}{r}\left(\frac{\chi_r+rb}{kT}\right)\right.$$

$$\left.-\left\{\tfrac{3}{2}+\sum\xi_r\frac{\chi_r+rb}{kT}\right\}\left\{\frac{\tfrac{3}{2}+\sum\xi\left(\frac{\chi_r+rb}{kT}\right)}{\sum r\xi_r}\right\}\right] \quad \ldots (33)$$

In the case where polymers of the type $(X)_2$ only exist the expression reduces to the following form :

$$C_v = Ak\left[\frac{15}{4}\frac{1+\xi}{2} + 3\xi\frac{b}{kT} + \tfrac{3}{2}(1-\xi)\frac{\chi+2b}{kT} + \left(\frac{b}{kT}\right)^2\xi + \frac{1-\xi}{2}\left(\frac{\chi_r+2b}{kT}\right)^2 - \left\{\tfrac{3}{2}+\xi\frac{b}{kT}+(1-\xi)\left(\frac{\chi+2b}{kT}\right)\right\}\left\{\frac{\tfrac{3}{2}+\xi\frac{b}{kT}+(1-\xi)\frac{\chi+2b}{kT}}{2-\xi}\right\}\right] \quad \ldots (33a)$$

Expression for $C_p + C_v$ *and* $\gamma = \frac{C_p}{C_v}$:

From equations (29) and (33), straightforwardly it follows that

$$C_p - C_v = Ak\left[-\frac{15}{2}\sum\xi_r - 3\sum\xi_r\frac{\chi_r+rb}{kT} - 5\left(\sum\xi_r\right)\left(\sum\xi_r\frac{\chi_r+rb}{kT}\right) - \left(\sum\xi_r\frac{\chi_r+rb}{kT}\right)\left(\sum\xi_r\frac{\chi_r+rb}{kT}\right) + \frac{1}{(\sum r\xi_r)}\left\{\tfrac{3}{2}+\sum\xi_r\left(\frac{\chi_r+rb}{kT}\right)^2\right\} + \left\{\tfrac{5}{2}\left(\sum\xi_r\right) + \sum\xi_r\frac{\chi_r+rb}{kT}\right\}(\sum r\xi_r)\left\{\tfrac{5}{2}\sum\xi_r + \sum\xi_r\frac{\chi_r+rb}{kT}\right\}\right] \quad \ldots (34)$$

and

$$\gamma = \left[-\frac{15}{4}\left(\sum\xi_r\right) - 5\left(\sum\xi_r\right)\left(\sum\xi_r\frac{\chi_r+rb}{kT}\right) - 2\left(\sum\xi_r\frac{\chi_r+rb}{kT}\right)\left(\sum\xi_r\frac{\chi_r+rb}{kT}\right) + \left\{\sum\xi_r\left(\frac{\chi_r+rb}{kT}\right) + 3\sum\xi_r\right\}\left\{\sum r\xi_r\right\}\left\{\tfrac{5}{2}\sum\xi_r + \sum\xi_r\frac{\chi_r+rb}{kT}\right\} + \sum\xi_r\left(\frac{\chi_r+rb}{kT}\right)^2\right] \times \left[\frac{15}{4}\left(\sum\xi_r\right) + 3\sum\xi_r\frac{\chi_r+rb}{kT} + \sum\xi_r\left(\frac{\chi_r+rb}{kT}\right)^2 - \frac{1}{(\sum r\xi_r)}\left\{\tfrac{3}{2}+\sum\xi_r\frac{\chi_r+rb}{kT}\right\}^2\right]^{-1} \quad \ldots (35)$$

VELOCITY OF PROPAGATION OF SOUND

From the well-known thermodynamic relation

$$v^2 = -\frac{\gamma V\left(\frac{\delta p}{\delta V}\right)_T}{\rho} = -\frac{\gamma V^2\left(\frac{\delta p}{\delta V}\right)_T}{Am} \quad \ldots (36)$$

(where v is velocity of sound, ρ=density), the velocity of propagation of sound in the gas, of the type considered here, is expressible in terms of T, V and degrees of dissociations. In the case where only polymers of the type $(X)_2$ can be formed, ξ, the degree of association can be determined from measurements of velocity of sound.

REMARKS ON THE DEDUCTION OF VELOCITY OF PROPAGATION OF SOUND

In deducing the equation (36) for velocity of propagation of sound, it has been tacitly assumed that all variations, considered, are reversible, *i.e.*, at every stage there is a state of thermodynamic equilibrium, and so, the variations are infinitely slow. In 1920, Einstein (1920) pointed out that during propagation of sound, variations, *i.e.*, propagations of expansions and compressions, are so rapid that the time is not sufficient for establishing thermodynamic, or better, chemical equilibria. According to him, for these processes, the gas is to be treated as a pure mixture. Thus, the equation (36), supplemented with equations (30) and (33), is expected to be valid to those cases, if any, where the velocity of chemical reactions are much greater than that of propagation of sound. Objection, as put forward by Einstein, can be raised for all sorts of thermodynamic variations (not only chemical reactions). In all thermodynamic methods for deduction of velocity of propagation of sound, the formula is deduced on considering reversible variations (which are infinitely slow processes) after using different laws, *viz.*, the equation of state, laws of thermodynamics, which are really valid for reversible variations, but the results obtained thereby are found to be in agreement with the experiments. So, the same agreement of the formula, obtained here, with experimental results is expected in wider range than that mentioned above.

CONCLUSION

According to Fowler (1936), the usual results of real gases can be obtained very easily by treating the assumbly of real gases as an assembly of point-molecules participating in associations. But, as shown here, the behaviours of isothermal compressibility, the coefficient of cubical expansion, etc. suggest that the thermodynamic behaviours of the assembly of associating molecules have a deviation from that of ideal gases, and the deviation is in the direction opposite to that of real gases.

The results, obtained in this present paper, give the relations of the compressibilities, coefficients of expansion, etc. with degree of associations. So, these are expected to be helpful for determinations of degree of associations in gas of the type considered in this paper from measurements of compressibilities, cubical expansions, etc., Now, from Vant-Hoff's (or Guldberg's) equations for mass-actions, degree of associations can be obtained as functions of temperature and pressure, so, ultimately all these compressibilities (isothermal or adiabatic), coefficient of cubical expansions etc., can be expressed (at least theoretically) in terms of temperature and pressure or temperature and volume as required.

ACKNOWLEDGMENTS

In conclusion, the author wants to express his hearty thanks and deep gratitude to Dr. S. C. Kar, Prof. S. N. Bose and Prof. N. R. Sen for their interest shown in the work and for their helpful discussions.

KHAIRA LEBORATORY OF PHYSICS,
UNIVERSITY COLLEGE OF SCIENCE & TECHNOLOGY,
92, UPPER CIRCULAR ROAD, CALCUTTA.

REFERENCES

Einstein, A., 1920, *Sitz. u. ber. Berlin*, pp. 380-85.
Fowler, R. N , 1930, Statistical Mechanics, pp. 157-61 and 214-89.
Epstein, P. S., 1947, Text-book of Thermodynamics, p. 379.